

Assemblies, crystal structures and properties of Zn^{II}, Cd^{II}, Cu^{II} and Ag^I supramolecular complexes with *trans*-1-(2-pyridyl)-2-(4-pyridyl) ethylene and 5-*tert*-butylisophthalic acid



Nan Sun, Yan Yan, Jing Chen *

College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, MOE Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Tianjin Normal University, Tianjin 300387, PR China

HIGHLIGHTS

- Four distinct Zn^{II}, Cd^{II}, Cu^{II} and Ag^I supramolecular complexes have been prepared.
- Structural diversification can be assigned to diverse coordination preferences of metal centers.
- Their thermal stability and solid state fluorescence have been studied.

ARTICLE INFO

Article history:

Received 8 January 2013

Accepted 2 April 2013

Available online 14 May 2013

Keywords:

Supramolecular complexes

Metal-directed assemblies

Secondary interactions

Thermal stability

Fluorescence

ABSTRACT

This work presents a series of four Zn^{II}, Cd^{II}, Cu^{II} and Ag^I supramolecular complexes based on *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (bpe) and 5-*tert*-butylisophthalic acid (5-*t*-buH₂ip). Complexes **1–4** have been prepared at ambient condition and characterized by IR, microanalysis, and powder X-ray diffraction (PXRD) techniques. Single-crystal X-ray diffraction indicates that complexes **1–3** display different 1D coordination motifs while **4** shows a tetranuclear structure. Moreover, extended 2D and 3D supramolecular architectures are further constructed in **1–4** via secondary interactions such as H-bonding and aromatic stacking. Notably, structural diversification for these complexes can be properly assigned to the central metal ions that have distinct coordination preferences. In addition, thermal stability and solid state fluorescence for these complexes have also been studied and discussed in detail.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

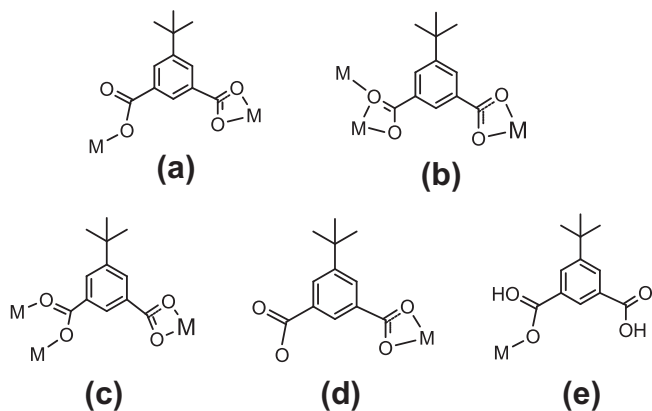
The rational design and assembly of metallosupramolecular complexes have attracted continuing interests in recent years, because of their diverse structures and potential applications in several areas such as optics, magnetism, catalysis, and gas storage [1–8]. From the standpoint of synthetic methodology, the access to such multi-component supramolecular systems mainly depends upon the selection of appropriate chemical subunits as building blocks [9–15]. In this regard, the organic ligands and metal ions play an important role in the construction of the final crystalline materials. Generally, polycarboxyl and polypyridyl ligands are selected as the reliable organic building blocks for structural assembly of these coordination materials [16–19]. In this context, polypyridyl ligands have been extensively studied to obtain various cationic polymeric networks with beautiful topologies, whereas the polycarboxyl ligands have been widely used to con-

struct neutral metal–organic frameworks (MOFs). Despite of the predesigned organic linkers and metal ions, to accurately predict and control the coordination architectures, especially in the mixed-ligand systems, still remains a considerable challenge at this stage [17]. In fact, specific reaction parameters such as solvent [20–22], reaction temperature [23,24] and pH value of the solution [25,26] may also significantly affect the formation of different thermodynamically favored crystalline products.

In this connection, it has been demonstrated that *trans*-1-(2-pyridyl)-2-(4-pyridyl)-ethylene (bpe) is a potential bifunctional ligand [27], where the 4-pyridyl group prefers to coordinate with the metal center, whereas the 2-pyridyl group has a tendency to serve as the H-bonding acceptor [28,29]. The aromatic dicarboxyl ligand 5-*tert*-butylisophthalic acid (5-*t*-buH₂ip), which has two carboxyl groups and a non-coordination group –C(CH₃)₃ at its 5-position, can affect the resulting crystalline frameworks because of the rich coordination modes of carboxyl groups (see Scheme 1) as well as the spatial and/or electronic effect of the non-coordinated group [30,31]. Therefore, we have prepared a series of new Zn^{II}, Cd^{II}, Cu^{II} and Ag^I coordination complexes based on bpe and

* Corresponding author. Tel.: +86 2223766556.

E-mail address: hxyxhj@mail.tjnu.edu.cn (J. Chen).



Scheme 1.

5-*t*-buH₂ip, aiming to explore the assembled law of such supramolecular systems. Moreover, their solid state properties including thermal stability and fluorescence have also been studied.

2. Experimental

2.1. Materials and general methods

All reagents and solvents for synthesis and analysis were commercially available and used as received. Fourier transform (FT) IR spectra (KBr pellets) were recorded on an AVATAR-370 (Nicolet) spectrometer. Elemental analyses of C, H, and N were taken on a CE-440 (Leemanlabs) analyzer. Thermogravimetric analysis experiments were performed on a TGA Q500 thermal analyzer in 25–800 °C (heating rate: 10 °C/min) under N₂ atmosphere with an empty Al₂O₃ crucible as the reference. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance diffractometer at 40 kV and 100 mA for a Cu-target tube ($\lambda = 1.5406 \text{ \AA}$). The calculated PXRD patterns were obtained from the single-crystal X-ray diffraction data by using PLATON. Fluorescence spectra of the solid samples were measured on a Cary Eclipse spectrofluorimeter (Varian) at room temperature.

2.2. Synthesis of complexes 1–4

[[Zn(bpe)₂(5-*t*-buip)](H₂O)₅]_n (1). A methanol solution (10 mL) of 5-*t*-buH₂ip (22.2 mg, 0.1 mmol) was mixed with an aqueous solution (10 mL) of Zn(OAc)₂·2H₂O (21.9 mg, 0.1 mmol) under stirring, to which a methanol solution (5 mL) of bpe (18.0 mg, 0.1 mmol) was added. The resultant solution was filtered and left to stand under ambient condition. Colorless block single crystals suitable for X-ray diffraction were produced after ca. 3 weeks with 39% yield (14.3 mg, based on bpe). Anal. Calcd. for C₃₆H₄₂ZnN₄O₉: C, 58.42%; H, 5.72%; N, 7.57%. Found: C, 58.64%, H, 5.69%, N, 7.68%. IR (cm⁻¹): 3444b, 2963w, 1609m, 1546m, 1382vs, 1281m, 963m, 821m, 733m, 691m, 547m.

[[Cd(bpe)(5-*t*-buip)(H₂O)](H₂O)]_n (2). The same synthetic method as that for **1** was used except that Zn(OAc)₂·2H₂O was replaced by Cd(OAc)₂·2H₂O (26.6 mg, 0.1 mmol). Colorless block crystals of **2** were produced with 34% yield (18.9 mg). Anal. Calcd. For C₂₄H₂₆CdN₂O₆: C, 52.33%; H, 4.76%; N, 5.09%. Found: C, 51.96%, H, 4.87%, N, 5.12%. IR (cm⁻¹): 3428b, 2963w, 1616s, 1571m, 1435m, 1362s, 1026w, 978w, 829m, 733w, 545w.

[Cu(bpe)₂(5-*t*-buip)]_n (3). The same synthetic approach as that for **1** was used except that Zn(OAc)₂·2H₂O was replaced by Cu(OAc)₂·H₂O (19.9 mg, 0.1 mmol). Green block crystals of **3** were produced with 54% yield (17.5 mg, based on bpe). Anal. Calcd. for C₃₆H₃₂CuN₄O₄: C, 66.70%; H, 4.98%; N, 8.64%. Found: C, 66.63%; H, 5.01%; N, 8.56%. IR (cm⁻¹): 1616s, 1567s, 1498w, 1430m, 1397w, 1353s, 1271w, 1219w, 970w, 879m, 779m, 719m, 544m.

[Ag₄(bpe)₄(5-*t*-buH₂ip)₂(5-*t*-buip)₂](H₂O)₂ (4). The same synthetic approach as that for **1** was used except that Zn(OAc)₂·2H₂O was replaced by Ag(OAc) (16.6 mg, 0.1 mmol). After the solution was left in darkness for 1 month, colorless block single crystals of **4** were obtained with 44% yield (23.1 mg). Anal. Calcd. for: C₉₆H₉₆Ag₄N₈O₁₈: C, 55.40%; H, 4.65%; N, 5.38%. Found: C, 55.63%; H, 4.56%; N, 5.42%. IR (cm⁻¹): 3423b, 2958 m, 2921s, 2852m, 2568w, 1691s, 1611m, 1544m, 1469m, 1438m, 1358w, 1325w, 1284m, 1160w, 1125w, 1008w, 973w, 832w, 64m, 692m, 549m.

2.3. X-ray single crystal diffraction

Single-crystal X-ray diffraction data for complexes **1–4** were collected on a Bruker Apex II CCD diffractometer at 296(2) K with

Table 1
Crystallographic data and structural refinement summary for complexes 1–4.

Compound reference	1	2	3	4
Chemical formula	C ₃₆ H ₄₂ ZnN ₄ O ₉	C ₂₄ H ₂₆ CdN ₂ O ₆	C ₃₆ H ₃₂ CuN ₄ O ₄	C ₄₈ H ₄₈ Ag ₂ N ₄ O ₉
Formula mass	740.11	550.87	648.20	1040.64
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
<i>a</i> (Å)	9.5243(5)	16.6123(12)	10.123(8)	11.859(8)
<i>b</i> (Å)	15.9002(9)	10.0034(7)	12.874(10)	14.933(10)
<i>c</i> (Å)	24.8762(14)	29.731(2)	14.181(12)	15.608(11)
α (°)	90.00	90.00	64.106(15)	112.504(11)
β (°)	93.4810(10)	104.5460(10)	88.638(16)	105.363(13)
γ (°)	90.00	90.00	76.091(15)	90.985(12)
Unit cell volume (Å ³)	3760.3(4)	4782.4(6)	1607(2)	2440(3)
F(000)	1552	2240	674	1060
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	4	8	2	2
No. of reflections measured	6639	4234	5623	8556
No. of independent reflections	5004	3869	2629	5921
<i>R</i> _{int}	0.0374	0.0182	0.0500	0.0249
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0404	0.0307	0.0550	0.0533
<i>wR</i> (<i>F</i> ²) (<i>I</i> > 2σ(<i>I</i>))	0.0969	0.0713	0.0733	0.1442
<i>R</i> 1 (all data)	0.0604	0.0348	0.1597	0.0808
<i>wR</i> (<i>F</i> ²) (all data)	0.1071	0.0732	0.0967	0.1609
Goodness of fit on <i>F</i> ²	1.034	1.096	1.020	1.045

Download English Version:

<https://daneshyari.com/en/article/7810895>

Download Persian Version:

<https://daneshyari.com/article/7810895>

[Daneshyari.com](https://daneshyari.com)